[D 7050.]

"Hydrolysis of Cane Sugar by d- and l-Camphor-β-Sulphonic Acid." By ROBERT JOHN CALDWELL, B.Sc., Clothworkers' Scholar, Chemical Department, City and Guilds of London Institute, Central Technical College.   Communicated by Professor H. E. ARMSTRONG, F.R.S.   Received June 16, 1904.

The study of the action of asymmetric hydrolytic agents on the sugars acquires interest from the fact that enzymes, which exhibit most remarkable activity as hydrolysts, are apparently all asymmetric in structure.   The only experiments of the kind made hitherto are those by Emil Fischer,[*] on the action of d- and l-camphoric acids on cane sugar, described in his memoir on the importance to Physiology of Stereochemistry.   No difference was detected; but as the experiments were made at 90° C. in sealed tubes, it was desirable to extend the inquiry and to operate under conditions more nearly comparable with those under which enzymes act.

At Professor Armstrong's suggestion, the acids selected for the purpose were the two isomeric acids of opposite activity prepared by direct sulphonation of d- and l-camphor by Reychler's method.   They are easily prepared and they act quickly, so that their action can be studied at atmospheric temperatures; moreover, as concentrated solutions can be used, even a small difference in their activity should not escape detection.   The inversion was carried out in a polarimeter tube enclosed in a jacket through which a flow of water was maintained varying in temperature by only $\pm$ 0·05° from 20·05° C. Readings of a_D were taken at intervals of 15 minutes.   The results obtained are entered in the following tables, in which a is the amount of cane sugar per litre of solution when the first reading was taken and $a - x$ the concentration of the solution, at other times t minutes after the first reading.   The strength of the acid in all cases was 0·488 gramme molecule per litre, as determined by titration with alkali.   The concentration of the sugar solution used was 17·1 per cent. (0·5 gramme molecule).   The rate of change was such that the inversion was about half completed at the end of six hours; the end point was determined in Cases I and II after 48 hours standing at 20° C.

Although there cannot have been any great difference in the conditions in the different experiments, the results must not all be included in one series, as the temperature regulator was readjusted after the first and after the fourth experiment; they are therefore to be considered in three sets, viz. : I: II, III, IV: V, VI, VII, VIII.

The first set gave $K = 10·02$ for the dextro acid and 9·95 for the

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[*] 'Zeits. Physiol. Chem.,' 1898, vol. 26, p. 83.

lævo acid; in the second set, the value obtained for the dextro acid was 9·87, that for the lævo acid being 9·99.

Slight variations in the temperature would account for such differences, as the influence of temperature on the rate of change is known to be very great. But even in these experiments the variations observed are small and not such as to suggest any substantial difference between the two acids. In the last set of observations, fully set forth in the table on p. 187, which there is every reason to regard as satisfactory, there is clearly no evidence of a difference in the activity of the d- and l-acids to be noticed.

The results, therefore, not only confirm the conclusion arrived at by E. Fischer, but are also in agreement with the observations of Marckwald and Chwolles,* that methylic d- and l-tartrates are hydrolysed with equal readiness by l-nicotine (at 17·5 and 40° C.). On the other hand, they are in remarkable contrast with the conclusions of Marckwald and McKenzie† and of McKenzie‡ that ethereal salts similarly derived from optically active isomeric compounds are both formed and hydrolysed at different rates. It is to be noticed, however, that the experiments of these chemists were carried out at relatively high temperatures and that they involved racemisation.

An experiment made with chlorhydric acid and cane sugar under conditions precisely similar to those prevailing in Experiments V—VIII, using a solution containing 17·6 per cent. (0·5 gramme molecule) of cane sugar and 0·486 gramme molecule of hydrogen chloride, gave the value $K = 11·18$.

Representing the activity of hydrogen chloride as 100, that of camphor-β-sulphonic acid is therefore 89·8, which is a value in accord with that assigned by Ostwald to ethylsulphonic acid, viz., 91·2.

In the preliminary stage of the inquiry, a comparison was also made of the action of chlorhydric acid and of d-camphor-β-sulphonic acid on milk sugar at 60°·1. The value obtained for the former was $K = 3·53$. § The values observed in the case of the camphor-acid were as follows :—

* ' Ber.,' 1898, vol. 31, p. 783.
† ' Ber.,' 1899, vol. 32, p. 3120.
‡ ' Chem. Soc. Trans.,' 1904, vol. 85, p. 378.
§ ' Roy. Soc. Proc.,' vol. 73, p. 532.

18 per cent. (0·5 gramme molecule) milk sugar, 0·400 gramme molecule
d-camphor-β-sulphonic acid.   Temperature, 60°·1.

Time in hours.	α_D	Per cent. hydrolysed.	$\dfrac{10^4}{t} \log_{10} \dfrac{a}{a-x}$.
0	20·90	—	—
8	21·73	14·9	[1·46]
16	21·93	18·5	0·93
22	22·37	26·4	1·01
44	23·45	45·8	1·01
72	24·30	61·0	0·95
95	24·88	71·5	0·96

Complete change ... 26·47   Mean ... 0·97

K (for normal acid) = 2·43.

Although possibly affected by a considerable error, on account of the
difficulty attending such observations at high temperatures, these
results appear to indicate that the activities of the two acids are by no
means the same towards cane sugar and towards milk sugar, being
about 100 : 90 in the one case and 100 : 70 in the other.   Sigmond has
already shown[*] in the case of cane-sugar and maltose, that although
sulphuric and oxalic acids have the same relative activity towards both
carbohydrates, chlorhydric acid is relatively more active towards
maltose : it appears, therefore, that cane sugar is less sensitive to attack
by chlorhydric acid than are other sugars.   The point is one which
deserves further investigation.

Although the experiments described in this note have given a negative
answer to the question considered, it is proposed to extend the inquiry
to other acids.

* 'Zeits. Phys. Chem.,' 1898, vol. 27, p. 390.

| | Dextro-acid. V. | | Laevo-acid. VI. | | Dextro-acid. VII. | | Laevo-acid. VIII. | |
Time.	α_D	$\dfrac{10^4}{t}\log_{10}\dfrac{a}{a-x}$	α_D	$\dfrac{10^4}{t}\log_{10}\dfrac{a}{a-x}$	α_D	$\dfrac{10^4}{t}\log_{10}\dfrac{a}{a-x}$	α_D	$\dfrac{10^4}{t}\log_{10}\dfrac{a}{a-x}$
15	26·65	—	16·70	—	26·70	—	16·73	—
30	25·68	9·86	15·67	[10·45]	25·67	[10·46]	15·68	[10·65]
45	24·70	10·08	14·75	10·06	24·75	10·07	14·73	10·31
60	23·80	9·99	13·82	10·07	23·80	10·15	13·85	10·06
75	22·88	10·09	12·93	10·06	22·95	10·01	12·93	10·14
90	22·00	10·13	12·07	10·05	22·05	10·11	12·03	10·21
105	21·18	10·09	11·25	10·03	21·22	10·09	11·18	10·22
120	20·22	10·08	10·43	10·06	20·38	10·16	10·47	10·02
135	19·57	10·14	9·65	10·06	19·65	10·07	9·67	10·06
150	18·88	10·04	8·88	10·09	18·85	10·14	8·92	10·06
165	18·15	10·05	8·18	10·05	18·17	10·07	8·18	10·08
180	17·45	10·05	7·47	10·06	17·45	10·10	7·50	10·05
195	16·75	10·08	6·82	10·03	16·72	10·16	6·82	10·05
210	16·12	10·06	6·17	10·03	16·07	10·16	6·17	10·05
225	15·48	10·07	5·47	10·11	15·40	10·15	5·57	10·01
240	14·85	10·08	4·92	10·04	14·80	10·18	4·93	10·05
255	14·27	10·08	4·32	10·05	14·22	10·17	4·33	10·06
270	13·65	10·14	3·73	10·07	13·67	10·15	3·83	9·99
285	13·12	10·12	3·20	10·05	13·15	10·11	3·25	10·02
300	12·60	10·11	2·73	9·99	12·53	10·20	2·70	10·04
315	12·05	10·14			12·05	10·17	2·22	10·00
345			1·18	10·06				
Complete change	− 2·33		−12·35		− 2·33		−12·35	
Mean		10·07		10·05		10·13		10·08